J. Synchrotron Rad. (1999). **6**, 81–86

Powder X-ray diffraction under extreme conditions of pressure and temperature

G. Fiquet[a]* and D. Andrault[b]

[a]Laboratoire de Sciences de la Terre – UMR5570, Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, 69364 Lyon CEDEX 07, France, and [b]Département des Géomatériaux, Institut de Physique du Globe de Paris, 4 Place Jussieu, 75252 Paris CEDEX 05, France. E-mail: gfiquet@ens-lyon.fr

(*Received 26 October 1997; accepted 7 January 1999*)

An important work has been carried out in the field of X-ray diffraction in obtaining accurate structural information from materials at extreme conditions of pressure and temperature. An experimental set-up combining a diamond-anvil high-pressure cell and a laser-heating technique has been installed at the high-pressure beamline ID30 at the ESRF (Grenoble) to study two major constituents of the Earth's deep interior: $MgSiO_3$ perovskite and iron. Experiments carried out on $MgSiO_3$ perovskite up to 86 GPa and over 2000 K yielded detailed structural information on this compound under these conditions and thus important constraints for the lower mantle mineralogical model, favouring a mixture of perovskite and magnesiowüstite. X-ray diffraction patterns recorded on imaging plates with micro-focused monochromatic radiation revealed a new high-temperature structure of iron above 40 GPa.

Keywords: powder diffraction; laser heating; diamond-anvil cells; $MgSiO_3$; perovskite; iron.

1. Introduction

The study of the deep Earth has been motivating generations of scientists who have to take up the experimental challenge given by the conditions existing at the centre of the Earth: 364 GPa and 6000 ± 500 K. The study of the propagation of elastic waves created by earthquakes is the only way to infer the density and compressibility profiles of our planet. The main problem remains in the determination of the chemical composition and crystalline structures existing in the deep Earth and which govern the Earth's global dynamics (thermal regime, convection drifts and plate tectonics, for example). To solve this problem, relationships have to be established between chemical composition, crystalline structure and specific volume over the whole range of pressures and temperatures existing within the Earth. X-ray diffraction is by far the ideal technique for the determination of equations of state and crystal structures. The high brilliance of synchrotron rings, coupled with advances in detector technology, has stimulated a rapid development of techniques for collecting data from the extremely small and heterogeneous samples studied in experimental geophysics (Haüsermann & Hanfland, 1996).

Some new developments in experimental techniques on synchrotron sources are now allowing significant progress to be made in the quality of crystal structure information at very high pressure and temperature. The introduction of the image-plate (IP) area detector, used with monochromatic synchrotron radiation for angle dispersive (AD) studies, has recently transformed the situation. Such AD diffraction techniques are now widely used for high-pressure experiments (*e.g.* Nelmes & McMahon, 1994), including diffraction at simultaneous high pressure and high temperature (Saxena *et al.*, 1995; Andrault *et al.*, 1997; Fiquet *et al.*, 1998). The work described in this paper is dedicated to the *in situ* X-ray diffraction study of laser-heated diamond-anvil cell samples, with a special emphasis on two major constituents of the deep Earth: $MgSiO_3$ perovskite and iron.

2. Experimental techniques

Extreme conditions of static pressure and temperature can be obtained on materials by combining laser heating with diamond-anvil cells (Ming & Bassett, 1974). Although high P–T conditions to 200 GPa and 6000 K have already been achieved using this technique (Boehler, 1993), very few experiments have been coupled to X-ray diffraction (Fiquet *et al.*, 1996). Difficulties in obtaining uniform heating, reliable temperature measurements and very high pressures restrict the dimensions of the samples to a few micrometres in thickness and a few tens of micrometres across. Two single-electrode bimorph mirrors were therefore installed at beamline ID30 of the ESRF to produce a bright monochromatic focal spot of ~10 μm × 15 μm (FWHM). X-ray beams of wavelengths ranging from 0.4 to 0.5 Å were selected from two phased undulators using a channel-cut Si(111) monochromator. This allowed us to collect for the first time AD diffraction data using imaging

plates on laser-heated diamond-anvil cell samples. These measurements were carried out using an experimental set-up especially designed for this purpose (Fiquet *et al.*, 1996). This experimental set-up is shown in Fig. 1 and consists of:

(i) a (TEM 00) CO_2 or multimode YAG laser-heating system to heat the samples in the diamond-anvil cell;

(ii) an optical set-up designed for on-line pressure and temperature measurements, and the direct observation and alignment of the sample on the X-ray beam spot;

(iii) a large-aperture diamond-anvil cell allowing *in situ* pressure and temperature measurements and full 4θ angle-dispersive data collection.

Full diffraction patterns were collected in ~5–10 min on IPs located 400 mm from the sample. The ring was operating with one-third filling and at a current between 200 and 160 mA. Two-dimensional patterns were integrated after geometric corrections using the program *FIT2D* (Hammersley, 1996).

3. Discussion

3.1. *$MgSiO_3$ perovskite*

The perovskite form of $(Mg,Fe)SiO_3$ is currently accepted as the dominant phase of the Earth's lower mantle, extending from 700 to 2900 km in depth (Mao *et al.*, 1977; Ito & Matsui, 1978). Consequently, the knowledge of its equation of state plays a crucial role in various fields of geophysics. It is, for instance, impossible to choose between a pure perovskite and a perovskite–magnesiowüstite (Mg,Fe)O model for the Earth's lower mantle on the basis of the existing data. *In situ* high-pressure high-temperature X-ray diffraction is certainly the only method available to constrain correctly the equation of state of perovskite and MgO in order to solve this important issue. Only two studies have been conducted so far in the stability field of the perovskite (Funamori & Yagi, 1993; Funamori *et al.*, 1996), and these experiments were carried out with a Drickamer-type cell and a multi-anvil press, respectively. Both used synchrotron radiation, but these volume measurements were made using the energy-dispersive (ED) technique up to 30 GPa and 2000 K.

We report new measurements of the equation of state of $MgSiO_3$ perovskite at pressures up to 86 GPa and temperatures up to 2700 K, thus extending the pressure and temperature field explored so far. Laser-heating techniques have been improved by the use of a high-power multimode IR YAG laser that allowed us to reach higher pressures. Data collection and transfer have been made much easier

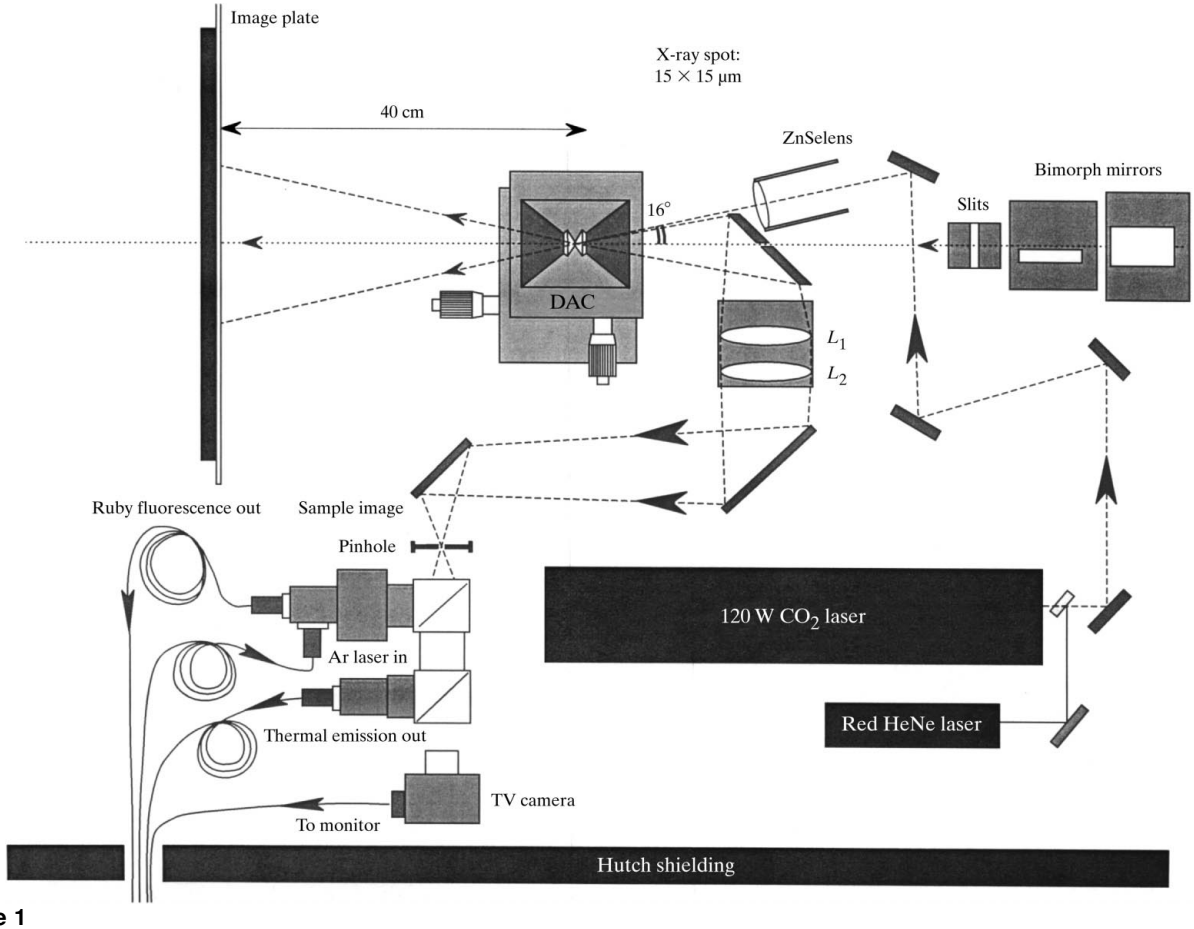

Figure 1
Experimental set-up at the ID30 high-pressure beamline (ESRF). The diamond-anvil cell front optical entrance is used for (i) access for the X-ray and IR laser beams and (ii) ruby fluorescence and blackbody measurements. The optical signals are conducted through optic fibres to the spectrometer. The X-ray diffraction pattern is collected on a two-dimensional IP detector.

and efficient owing to the on-line IP reader 'FastScan' available on ID30 (Thoms *et al.*, 1998). Silicate perovskite $MgSiO_3$ samples were synthesized from synthetic $MgSiO_3$ enstatite crystals or synthetic $MgSiO_3$ glass mixed with platinum powder. These starting materials were loaded into a large-aperture diamond-anvil cell and transformed at high pressure and high temperature either with a CO_2 or a YAG IR laser, depending of the pressure-transmitting medium used. Temperatures were measured from the analysis of the thermal emission of the samples, recorded during the X-ray diffraction pattern acquisition. Pressure conditions were inferred from the PVT equation of state of platinum, used as an internal pressure calibrant (Jamieson *et al.*, 1982).

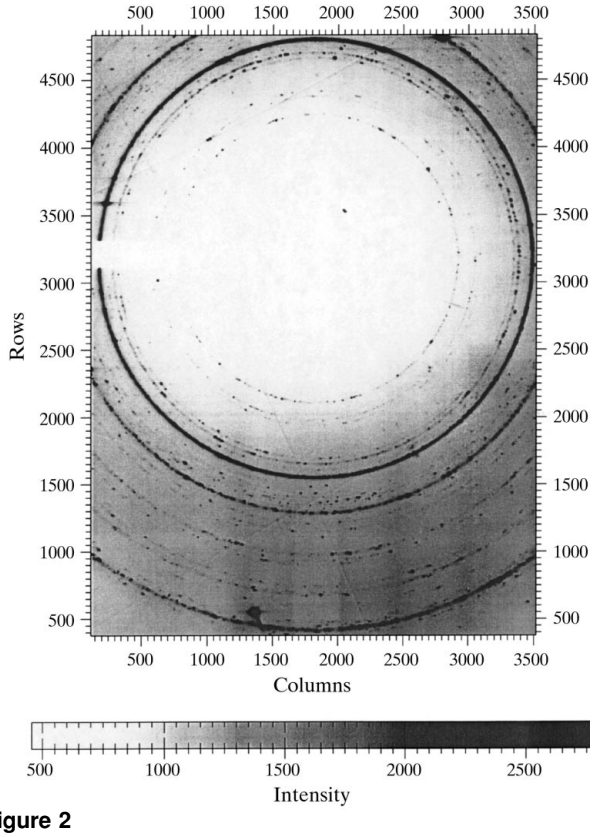

Figure 2
Two-dimensional diffraction pattern recorded on a mixture of platinum and $MgSiO_3$ sample at 79.9 GPa and 1680 K. On-line reading imaging-plate detector: FastScan. Exposure time = 10 min.

Le Bail profile refinements were applied to the diffraction patterns in order to obtain reliable high-pressure high-temperature cell parameters for $MgSiO_3$ as well as for the pressure calibrant, after correction and integration of images collected over a few minutes (Fig. 2). One of the most remarkable results is that Rietveld structural refinements could be achieved on selected patterns at these extreme pressure and temperature conditions (Fig. 3), thus providing for the first time fine structural information on these compounds. It is, for instance, possible to show that the internal distortion of the SiO_6 octahedra increases with increasing pressure.

Data analysis allowed us to identify a set of thermoelastic parameters, in order to constrain the compositional model of the Earth's lower mantle. Assuming that the thermoelastic parameters obtained from this study are applicable to perovskites with moderate iron content, the comparison of the density and K_T (bulk modulus) profiles calculated for a pure perovskite model and for a seismological global Earth model [Preliminary Reference Earth Model (PREM); Dziewonski & Anderson, 1981] indicates that a pure perovskite lower mantle is very unlikely, thus corroborating previous experimental results (Wang *et al.*,

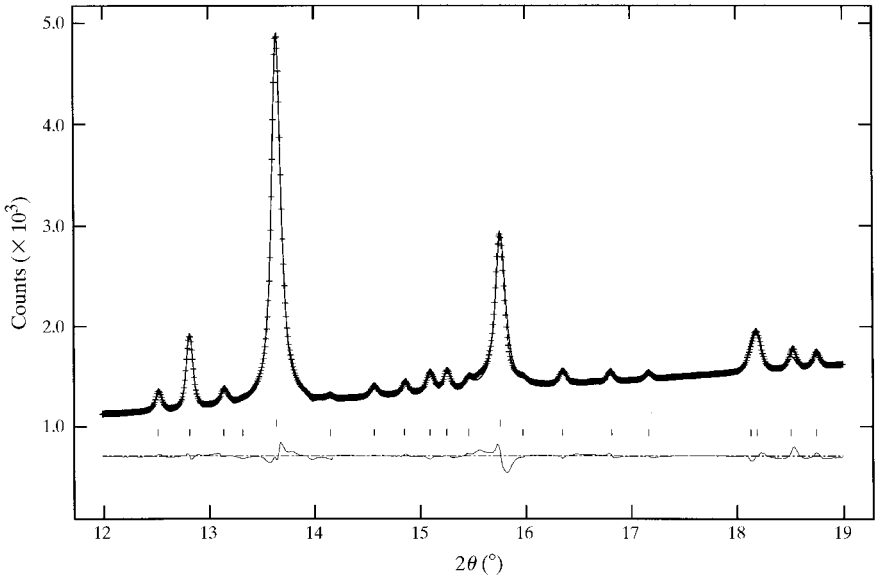

Figure 3
Rietveld full structure refinement of a diffraction spectrum of $MgSiO_3$ at 79.7 GPa and 1680 K integrated from an image plate exposed for 10 min using a monochromatic beam (0.5087 Å) focused to 10 × 20 μm^2. Space group *Pbnm*, a = 4.4456 (4), b = 4.6648 (3), c = 6.4540 (4) Å, R_{wp} = 1.28% and $R(F^2)$ = 6.3% for $MgSiO_3$ perovskite phase. Sample reflections (lower ticks) are mixed with reflections from platinum, the internal pressure calibrant (upper ticks).

1994; Utsumi *et al.*, 1995; Funamori *et al.*, 1996). We obtain a very good match with PREM density and K_T profiles for a mixture of 83 vol.% $(Mg_{0.93},Fe_{0.07})SiO_3$ perovskite and 17 vol.% $(Mg_{0.79}Fe_{0.21})O$ magnesiowüstite (Fiquet *et al.*, 1998).

3.2. *Iron*

As iron is the dominant constituent of the Earth's core, information on its behaviour at high pressure and high temperature is fundamental in Earth sciences. However, despite numerous studies on this subject [see Anderson (1995) for a review], there is still much uncertainty about the actual structure of iron under the pressure and temperature conditions relevant to the core. The accurate determination of the phase diagram of this element is indeed an experimental challenge because of the extreme P–T conditions involved. For example, recent X-ray diffraction experiments below 100 GPa have led to conflicting results about the structure of the new iron β-phase (Saxena *et al.*, 1995; Yoo *et al.*, 1995). The region of the phase diagram below 100 GPa, which only a few years ago was thought to be simple, must now be regarded as complicated, and clearly requires new experiments for clarification. As mentioned by Anderson (1995), the final choice between the ε-phase and the γ-phase for the core depends on the outcome of future studies aiming at proving the existence of the β-phase and identifying its crystallographic structure.

The iron phase diagram has thus been studied up to 100 GPa and 2700 K. The results of this study introduce strong constraints on the iron structure at high pressure and high temperature (Andrault *et al.*, 1997). We significantly improved both resolution and reliability of the diffraction peak intensities by using the combination of monochromatic X-radiation and IP detector. Fig. 4 shows typical two-dimensional images recorded on an iron foil compressed in Al_2O_3 at 44.6 GPa at two temperatures, *i.e.* room temperature and 1965 (60) K. The continuous rings represent the pressure-transmitting medium Al_2O_3 reflections whereas the spotty discontinuous line is typical of this type of sample. The left-hand side of Fig. 4 represents a diffraction pattern of the ε h.c.p.-phase of iron and the right-hand side points out the slight modifications of this structure at high temperature, denoted by arrows in the figure. A similar spectrum recorded during laser heating at 2125 $\pm$ 70 K at 44.6 GPa was used for a structure refinement of iron (see Fig. 5). This pattern suggests a structure different from h.c.p. iron (ε) reported so far at these pressure and temperature conditions (Yoo *et al.*, 1995) or from the *d*-h.c.p. structure as proposed by Saxena *et al.* (1995). The space group was instead determined to be *Pbcm*, with an atomic topology close to that of ε-h.c.p. iron. The structure is also closely related to the lower-pressure high-temperature polymorph γ-iron (f.c.c.). The high-temperature polymorph appears unquenchable in a pressure range explored to 80 GPa.

To avoid any artifact related to this iron phase transformation in corundum, we also checked the formation of this orthorhombic phase above 80 GPa using SiO_2 as the pressure-transmitting medium. At 100 GPa, difficulties were encountered in insulating the sample from the diamonds, and it was therefore difficult to produce *in situ* X-ray spectra during stable laser heating. However, quenched patterns were recorded at this pressure after laser

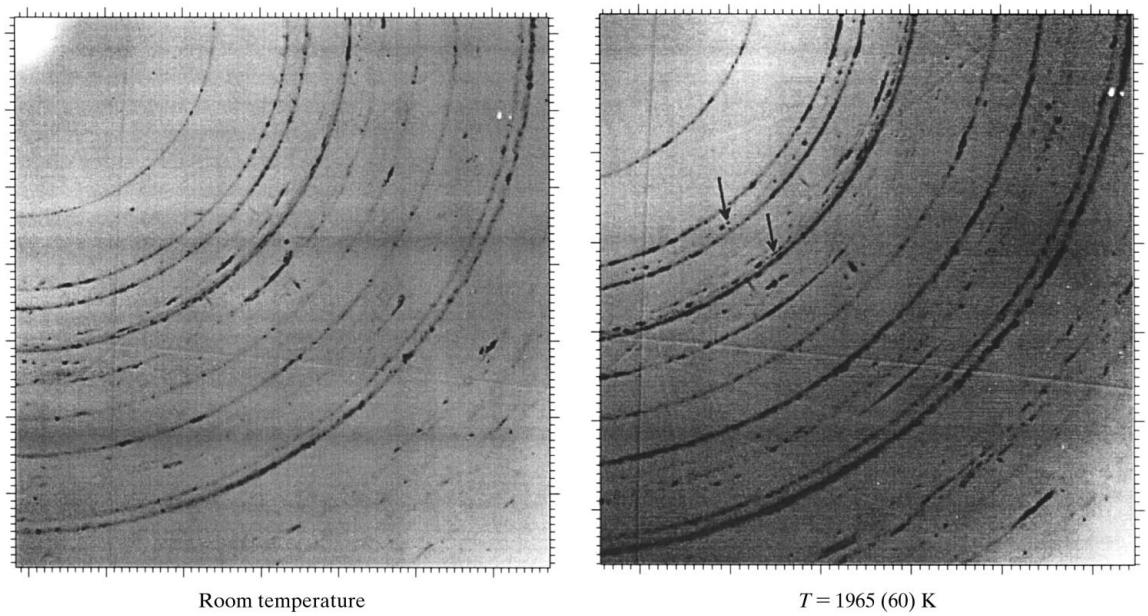

Figure 4
Two-dimensional diffraction patterns of iron recorded in a diamond-anvil cell at 44.6 GPa at room temperature (left) and at 1965 (60) K (right). λ = 0.4245 Å. Exposure time = 10 min.

heating up to ~2500 K (Fig. 6). It clearly shows the splitting of the 100 and 101 lines of the h.c.p. lattice, which again provides evidence of a phase transformation for iron at high pressure and temperature. All diffraction lines are perfectly explained by an orthorhombic lattice similar to that previously observed, thus indicating that the pressure-transmitting medium itself is clearly not responsible for the structural changes that take place in iron at high pressure and high temperature. At variance with the results obtained at moderate pressures, however, the structure of the high-temperature polymorph is now preserved when quenched from high temperature at megabar pressures, suggesting a negative Clapeyron slope between the high-temperature orthorhombic and low-temperature ε phases. At this pressure, the orthorhombic lattice is found to be about 1% denser than ε-iron, with values of 10.76×10^3 and 10.85×10^3 kg m^{-3}, respectively.

4. Conclusions

The quality of the data obtained at third-generation sources such as the ESRF has drastically improved the level and quality of structural information on high-pressure phases. Shortcomings associated from recrystallization of the samples at high temperature or strong preferred orientation have been largely overcome with the use of two-dimensional IP detectors, thus yielding more reliable relative intensities than conventional ED methods. ED diffraction suffers from an intrinsic lower resolution and from a bad spatial coverage, which is an important problem when considering the 'spotty' aspect of most 'extreme conditions' diffraction patterns. The results obtained here show, for example, the strong constraints brought on the mineralogical model of the Earth's lower mantle or on the structure of iron inside the Earth's core.

These results would not have been obtained without the efforts of many people. Firstly, thanks are due to the people who participated in the experiments: A. Dewaele, F. Visocekas, T. Charpin and Ph. Gillet. We are also particularly

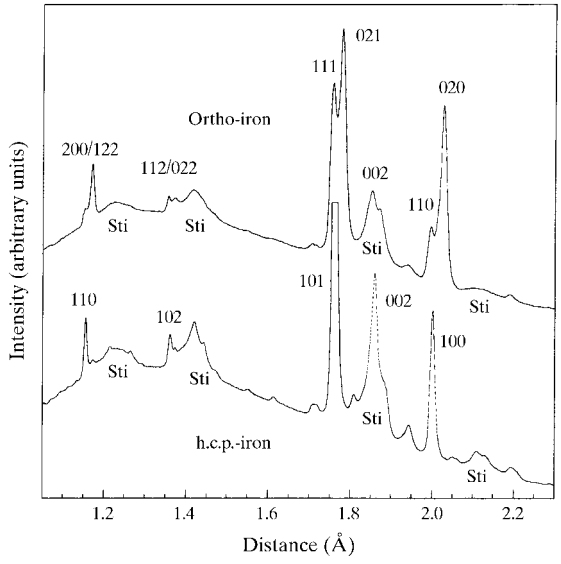

Figure 6
Diffraction spectra of h.c.p. and orthorhombic iron recorded at 100 GPa in an SiO_2 pressure-transmitting medium (denoted by Sti). The 101 Bragg line of ε-iron (bottom spectrum) was truncated for clarity (intensity up to 20000 counts). The top spectrum was recorded after laser heating at ~2500 K. It clearly shows the splitting of the 100 and 101 ε-iron lines, thus providing evidence of the phase transition towards the orthorhombic phase (after Andrault *et al.*, 1997).

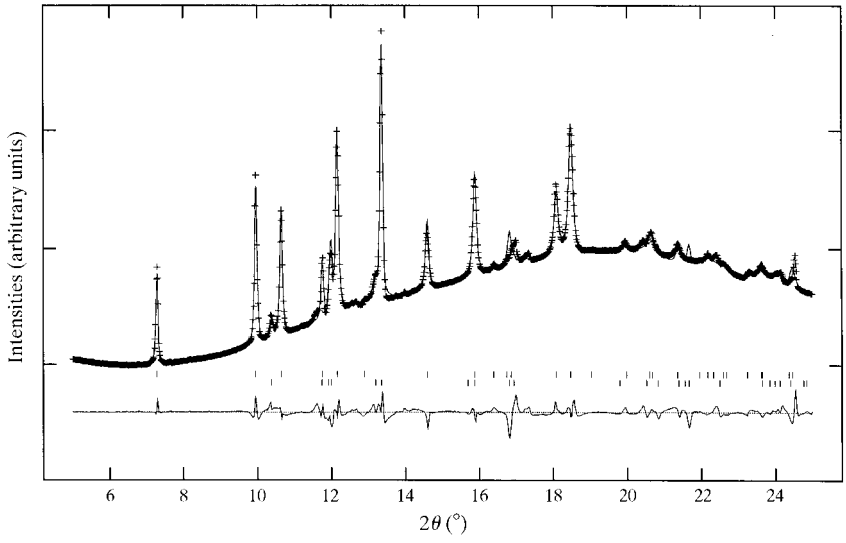

Figure 5
Full structure refinement of a spectrum recorded during laser heating at 2125 (70) K under a pressure of 44.6 GPa. We obtained a very good agreement of the spectral intensities [R_{wp} = 1.11% and $R(F^2)$ = 5.7% for the iron phase] using an orthorhombic cell [a = 2.3460 (3), b = 4.1445 (5), c = 4.0615 (8) Å], space group *Pbcm* (57), and iron location at (0.239, 0.472, 0.25). Displayed are the observed, calculated and difference spectra. The Fe pattern (lower ticks) is associated with reflections from the Al_2O_3 pressure-transmitting medium (upper ticks).

grateful to D. Häusermann, M. Kunz, S. Bauchau and M. Hanfland from the ESRF for their help at the ID30 beamline, and the ECC (ESRF Extreme Conditions Consortium) for the loan and maintenance of the YAG multimode IR laser.

References

Anderson, O. L. (1995). *Rev. Geophys.* (supplement to *US Natl Rep. Int. Union Geod. Geophys. 1991–1994*), pp. 429–441.

Andrault, D., Fiquet, G., Visocekas, F., Kunz, M. & Häusermann, D. (1997). *Science*, **278**, 831–834.

Boehler, R. (1993). *Nature (London)*, **363**, 534.

Dziewonski, A. M. & Anderson, D. L. (1981). *Phys. Earth Planet. Int.* **25**, 297–356.

Fiquet, G., Andrault, D., Dewaele, A., Charpin, T., Kunz, M. & Haüsermann, D. (1998). *Phys. Earth Planet. Int.* **105**, 21–31.

Fiquet, G., Andrault, D., Itié, J. P., Gillet, Ph. & Richet, P. (1996). *Phys. Earth Planet. Int.* **95**, 1–17.

Funamori, N. & Yagi, T. (1993). *Geophys. Res. Lett.* **20**(5), 387–390.

Funamori, N., Yagi, T., Utsumi, W., Kondo, T., Uchida, T. & Funamori, M. (1996). *J. Geophys. Res.* **101**(B4), 8257–8269.

Hammersley, J. (1996). *FIT2D*. ESRF, Grenoble, France.

Haüsermann, D. & Hanfland, M. (1996). *High Press. Res.* **14**, 223–234.

Ito, E. & Matsui, Y. (1978). *Earth Planet. Sci. Lett.* **38**, 443–450.

Jamieson, J. C., Fritz, J. N. & Manghnani, M. H. (1982). *High Pressure Research in Geophysics*, edited by S. Akimoto & M. H. Manghnani, pp. 27–48. Boston: Reidel.

Mao, H. K., Yagi, T. & Bell, P. M. (1977). *Carnegie Institute Washington Yearbook 76*, pp. 502–504. Carnegie Institute, Washington DC, USA.

Ming, L. C. & Bassett, W. A. (1974). *Rev. Sci. Instrum.* **45**, 1115.

Nelmes, R. J. & McMahon, M. I. (1994). *J. Synchrotron Rad.* **1**, 69–73.

Saxena, S. K., Dubrovinsky, L. S. & Häggkvist, P. (1995). *Science*, **269**, 1703–1704.

Thoms, M., Häusermann, D., Bauchau, S., Kunz, M., LeBihan, T., Mezouar, M. & Strawbridge, D. (1998). *Nucl. Instrum Methods*, A**413**, 175.

Utsumi, W., Funamori, N., Yagi, T., Ito, E., Kikegawa, T. & Shimomura, O. (1995). *Geophys. Res. Lett.* **22**(9), 1005–1008.

Wang, Y., Weidner, D. J., Liebermann, R. C. & Zhao, Y. (1994). *Phys. Earth Planet. Inter.* **83**, 13–40.

Yoo, C. S., Akella, J., Campbell, A. J., Mao, H. K. & Hemley, R. J. (1995). *Science*, **270**, 1473–1475.